# (19) World Intellectual Property Organization International Bureau



# 

# (43) International Publication Date 31 July 2003 (31.07.2003)

### **PCT**

# (10) International Publication Number WO 03/062249 A3

- (51) International Patent Classification<sup>7</sup>: C07F 3/00, 3/02
- (21) International Application Number: PCT/GB03/00163
- (22) International Filing Date: 16 January 2003 (16.01.2003)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0201141.9

18 January 2002 (18.01.2002) GB

- (71) Applicant (for all designated States except US): IC IN-NOVATIONS LTD [GB/GB]; 47 Prince's Gate, Exhibition Road, London SW7 2QA (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): MARSHALL, Edward [GB/GB]; 8 Miller Road, Croydon, Surrey CRO 3JY (GB). SEGAL, John [GB/GB]; 15 The Jinnings, Welwyn Garden City, Hertfordshire AL7 4QB (GB). GIBSON, Vernon, Charles [GB/GB]; Flat 2, 46 Prince's Gate, Exhibition Road, London SW7 2QA (GB).

- (74) Agents: CLYDE-WATSON, Zoe et al.; D Young & Co., 21 New Fetter Lane, London EC4A 1DA (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### **Declaration under Rule 4.17:**

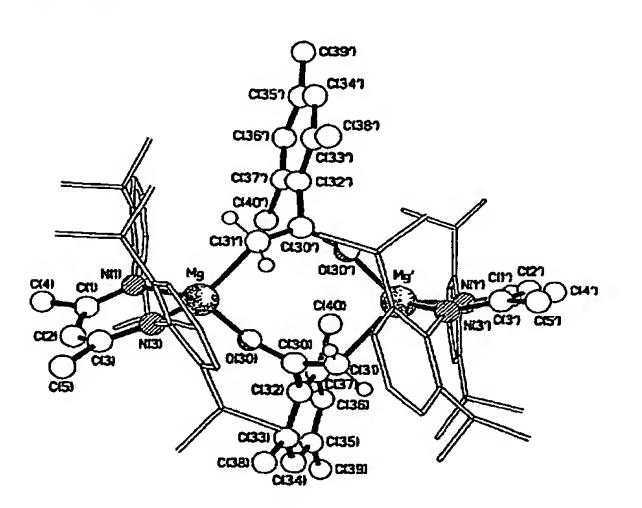
- of inventorship (Rule 4.17(iv)) for US only

### Published:

- with international search report

[Continued on next page]

### (54) Title: COORDINATION COMPLEX



$$L_2 \xrightarrow{L_1} X$$
 (1)

VO 03/062249

(57) Abstract: The present invention provides a complex of formula (I) wherein M is Ca, Mg, Ba or Sr,  $L_1$  is selected from  $R^1O$ ,  $R^2S$ ,  $R^3R^4N$ ,  $R^5R^6P$ , a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where  $R^{1-6}$  are each independently H or hydrocarbyl;  $L_2$  is selected from  $R^7R^8O$ ,  $R^7R^8S$ ,  $R^7R^8R^9N$ ,  $R^7R^8C=NR^9$ ,  $PR^7R^8R^9$ , and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, Where  $R^{7-9}$  are each independently H or a hydrocarbyl group; or  $L_1$  and  $L_2$  are linked to form a bidentate ligand;  $L_3$  is absent or is a solvent molecule, or a neutral ligand as defined for  $L_2$ , wherein  $L_3$ may be the same or different to  $L_2$ ; or  $L_3$  is linked to a further metal center; or  $L_1$ ,  $L_2$  and  $L_3$  are linked to form a tridentate ligand; and X is an alkyl group, an aryl group, an aryloxide, an amide group, or an enolate group of formula  $R^{10}$   $R^{11}C=CR^{12}O$ -, wherein  $R^{10-12}$  are each independently H or hydrocarbyl; with the proviso that when  $L_1$  and  $L_2$  are  $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}$  and M is magnesium, X is other than Me or  $^1Bu$ .

## WO 03/062249 A3



— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(88) Date of publication of the international search report:

27 November 2003

Interna | Application No GB 03/00163

A CLA	SSIF	CATION OF	SUBJECT	MATTER	
IPC	7	C07F3	/00	C07F3	/02

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 CO7F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, BEILSTEIN Data

Category °	Citation of document, with indication, where appropriate, of the relevant passages	1-6,15, 21	
X	GIBSON, VERNON C. ET AL: "Novel Mono-alkyl Magnesium Complexes Stabilized by a Bulky.betaDiketiminate Ligand: Structural Characterization of a Coordinatively Unsaturated Trigonal System" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (2000), 122(29), 7120-7121, XP002234846 Scheme 1: compounds 2-4		
X X	page 7120, column 2; figures 1-3 page 7121, column 2, paragraph 3 page 7121, column 1	23,24,26 32	
X	EP 0 747 405 A (BRIDGESTONE CORPORATION, JAPAN) 11 December 1996 (1996-12-11) page 5, line 35 - line 55	1,2	
<b>⟨</b>	page 11, line 1 -page 16	23	

	-/		
X Further documents are listed in the continuation of box C.	χ Patent family members are listed in annex.		
"A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier document but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report		
25 September 2003	0 1 10. 2003		
Name and mailing address of the ISA	Authorized officer		
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Richter, H		

Intern: Application No GB 03/00163

		GB 03/00163
	Citation of document, with indication where appropriate of the relevant passages	Relevant to claim No.
Category °	Citation of document, with indication, where appropriate, of the relevant passages	i televant to claim ito.
X	WEEBER, ARMIN ET AL: "Homoleptic and Heteroleptic Barium Benzyl Complexes: Synthesis and Reactivity as Initiators for Anionic Styrene Polymerizations" ORGANOMETALLICS (2000), 19(7), 1325-1332,	1-3
<b>X</b> .	XP000920607 compound 6: (C5Me5)2Ba.2THF; page 1327, column 2 barium bis(2,4,6-tri-tertbutyl phénolate.2THF page 1330, column 2, line 32 - line 33	1-3
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; RAMIREZ, FAUSTO ET AL: "Preparative chemistry of organic magnesium oxyanion complexes. 5. Aroxide complexes" retrieved from STN Database accession no. 91:32007 XP002234848 abstract; figures 21,22 & SYNTHESIS (1979), (1), 71-4,	1-3
X	DATABASE CROSSFIRE BEILSTEIN [Online] Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Tetrahedron, 53; 22; 7671-7688, 1997 DESIMONI, G. ET AL.: Database accession no. BRN 7792064 XP002234867 abstract	1-4,8
<b>A</b> ' .	ZHONG, ZHIYUAN ET AL: "A Novel and Versatile Calcium-Based Initiator System for the Ring-Opening Polymerization of Cyclic Esters"  MACROMOLECULES (2001), 34(12), 3863-3868, XP002234847  Ca[NSiMe3)2]2(THF)2  page 38633 -page 3867; table 1	1-3,17,
<b>A</b> .	XVIIth International Conference on Organometallic Chemistry; Munich, August 16-21, 1998, Part 1 Poster Session A; D.Schramm, W.Kläui "Synthesis of Cationic Hydrotris(pyrazolyl)borate Zirconium Compounds" XP002249590 A 150 abstract	9,14

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
· · · · · · · · · · · · · · · · · · ·
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
see additional sheet
1. X As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.
No protest accompanied the payment of additional search fees.

### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 4-8,31-33; partially: 1-3,15-30,34,35

Bidentate complexes falling within formula I according to claim 1, their preparation and use

- 1.1. Claims: partially 1-3,15-30,34,35
  Monodentate complexes of formula I and their use
- 2. Claims: 9-14, partially 1-3,15-30,34,35

Tridentate complexes falling within formula I according to claim 1 and their use

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

Interr | Application No PO | 3 / 00163

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0747405 A	11-12-1996	US 5610227 A CA 2178145 A1 DE 69601327 D1 DE 69601327 T2 EP 0747405 A1 ES 2126353 T3 JP 9003111 A	11-03-1997 08-12-1996 25-02-1999 27-05-1999 11-12-1996 16-03-1999 07-01-1997